

### STATUS OF THE CLAIMS

Claims 1-8 and 10-22 were pending.

Claims 1 and 10-12 have been rejected under 35 U.S.C. § 102(b) as being anticipated by Bell, et al. (US 4,504,509) and Mizoguchi, et al (US 5,362,510).

Claims 2-6 have been rejected under 35 U.S.C. § 103(a) as being unpatentable over Bell, et al. (US 4,504,509) in view of Richards, et al. (US 4,035,235).

Claims 8 and 13-22 have been rejected under 35 U.S.C. § 103(a) as being patentable over Bell, et al. (US 4,504,509) in view of Wu et al. (US 5,648,110).

Claims 1, 2 and 7 have been rejected under 35 U.S.C. § 103(a) as being patentable over Shi, et al. (US 2003/0099744).

Claims 1, 3, 4, 8, 14 and 20 have been amended.

Claims 1-8 and 10-22 are presented for reconsideration.

## REMARKS

Claims 1, 3, 4, 8, 14 and 20 have been amended to read on a succinated starch derivative. Descriptive basis for this may be found in the specification, e.g., Example 1. Applicants respectfully request entry of Modified Starches: Properties and Uses, O.B. Wurzburg, Editor, CRC Press, Inc. Florida (1986) which supports that starch succinates (half-esters) are also known as starch succinate derivatives (see underlined portions).

Claims 1 and 10-12 have been rejected under 35 U.S.C. § 102(b) as being anticipated by Bell, et al. (US 4,504,509) and Mizoguchi, et al. (US 5,362,510). Bell discloses a liquid batter for use in coating foodstuffs which comprises ungelatinized, highly crosslinked, high amylose starch. The crosslinking agent may be selected from the group specified in col. 3. The Examiner notes that one of these reagents is succinic anhydride. The skilled artisan would understand that crosslinking, such as with succinic anhydride, is a process in which starch is treated with a poly-functional reagent so that two or more starch polymer chains are chemically linked. In contrast, the current invention claims a composition which comprises a starch succinate ester in which at least one of the hydroxyl groups on a single starch polymer is replaced by an ester group. This is not a *crosslinked* starch but a *substitution* in which the starch gains a substituent. Thus, Bell teaches starch polymers that are linked together while the present invention teaches starches which are not linked together.

Mizoguchi teaches starches which are crosslinked with epichlorohydrin, but states that they may be crosslinked with esterifying agents such as succinic anhydride.

The Examiner was not persuaded that the skilled artisan would understand the term "starch succinate" refers to succinic acid monoester as opposed to the succinate crosslinked starches of Bell and Mizoguchi. As evidenced in Wurzburg reference (enclosed herewith), starch succinates or starch half esters are also known as starch succinate derivatives.

The Examiner also states that Example 1 does not state that the ester is starch succinate mono-esters (half esters). However, the skilled artisan understands that whether a starch will form a derivative (half ester) or a crosslink depends upon the reaction. As stated in the Billmers declaration (of record), "the patent application

“discloses a starch ester; that is, a single starch polymer in which one of the hydroxyl groups has been substituted with an ester group. This is based upon the description, particularly the examples.” Billmers then continues to specifically point out the conditions which lead to his conclusion. Thus, it is clear that both Bell and Mizoguchi disclose crosslinked starches while the present invention discloses a starch derivative and, as the starches are different, the rejection has been overcome.

Claims 2-6 have been rejected under 35 U.S.C. § 103(a) as being unpatentable over Bell, et al. (US 4,504,509) in view of Richards, et al. (US 4,035,235). As explained above, Bell does not disclose using a half-ester or starch succinate derivative, but a crosslinked starch. The Examiner then uses Richards to teach that starch derivatives may be converted. However, as Bell does not teach the presently claimed starches, this rejection has been overcome.

Claims 8 and 13-22 have been rejected under 35 U.S.C. § 103(a) as being patentable over Bell, et al. (US 4,504,509) in view of Wu et al. (US 5,648,110). As explained above, Bell does not disclose using a half-ester or starch succinate derivative, but a crosslinked starch. The Examiner then uses Wu to teach that adding a different type of starch in addition to the main starch component. However, this does not cure the deficiency of Bell and the rejection is therefore overcome.

Claims 1, 2 and 7 have been rejected under 35 U.S.C. § 103(a) as being patentable over Shi, et al. (US 2003/0099744). Shi discloses glazing food using a converted starch. The starch may be modified using any chemical modification, specifying that particularly useful starches are acetylated, hydroxyalkylated, phosphorylated, succinated and substituted succinate derivatives. However, modification is only an optional step and succinated starch esters just one of the possible modifications with none of the examples showing such succinated starches. The Examiner states that the point of applying before frying or after frying is not germane to the issue at hand because the claims are directed to the food product not making it. Applicants respectfully disagree. Claim 1 as written is a product by process claim in that the starch succinate derivative is “adhered directly on the food portion to form a coated food portion which is subsequently fried or par-fried.”

The order of the step results in a different product as if the food portion is fried or par-fried and then the starch succinate derivative is adhered to the fried/par-fried food, the product will have a higher fat content. Thus, not only does the order of these steps change the product, but the order also distinguishes the present invention from Shi, overcoming the rejection.

In view of the foregoing, Applicant submits the Application is now in condition for allowance and respectfully requests early notice to that effect. Election by the Applicants not to address each and every statement made by the Examiner does not imply agreement with any unaddressed statement.

Respectfully submitted,



Karen G. Kaiser  
Attorney for Applicants  
Reg. No. 33,506

National Starch LLC  
10 Finderne Avenue  
Bridgewater, NJ 08807  
(908) 575-6152

Dated: 14 July 09

78313

# Modified Starches: Properties and Uses

Editor

**O. B. Wurzburg, M.S.**

Consultant

National Starch and Chemical Corp.  
Bridgewater, New Jersey



CRC Press, Inc.  
Boca Raton, Florida

**Library of Congress Cataloging-in-Publication Data**

Properties and uses for modified starches.

Includes bibliographies and index.

1. Starch. I. Wurzburg, O. B. II. Cremer,  
Charles W.

QD321.P896 1986 547.7'82 86-13674  
ISBN-0-8493-5964-3

This book represents information obtained from authentic and highly regarded sources. Reprinted material is quoted with permission, and sources are indicated. A wide variety of references are listed. Every reasonable effort has been made to give reliable data and information, but the author and the publisher cannot assume responsibility for the validity of all materials or for the consequences of their use.

All rights reserved. This book, or any parts thereof, may not be reproduced in any form without written consent from the publisher.

Direct all inquiries to CRC Press, Inc., 2000 Corporate Blvd., N.W., Boca Raton, Florida, 33431.

© 1986 by CRC Press, Inc.

International Standard Book Number 0-8493-5964-3

Library of Congress Card Number 86-13674  
Printed in the United States

## I. INTRODUCTION

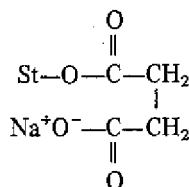
This chapter is divided into three sections:

1. Starch succinates which are prepared by simply reacting starch with succinic anhydride
2. Alkenyl succinates, resulting from the reaction of substituted succinic anhydride in which the substituent is an alkyl or alkenyl group
3. Sulfosuccinates, which result from the saturation of the double bond in starch maleate esters with sodium bisulfite or from the reaction of starch with sulfosuccinic anhydride or its alkyl or alkenyl substituted form

## II. STARCH SUCCINATES

## A. Preparation

Succinic anhydride reacts with starch to form the half-ester. The structural formula of the product of the reaction can be represented as follows:



The techniques reported in the literature to prepare starch succinate derivatives are many. It is possible to react all the hydroxyl groups of the starch molecule with succinic anhydride using pyridine as the medium.<sup>1</sup> A starch succinate with a high degree of substitution (DS) can also be prepared in glacial acetic acid containing sodium acetate at 100°C.<sup>2</sup> As is the case with other derivatives, succinic anhydride will react with starch in the granular form as well as in the cooked form. Most reactions, though, are carried out in the granular form. There is a limit, however, as to how much succinic anhydride can be reacted with granular starch. Above a 3% treatment level, the granules swell to such a degree that filtration becomes very difficult. This is due to the highly hydrophilic nature of the alkaline salt form of the carboxylic acid group which takes up a lot of water thus causing the granule to swell. Starch succinate derivatives are cleared for food use by the U.S. Food and Drug Administration (FDA) up to a 4% treatment level.<sup>7</sup>

## B. Properties

Starch succinates are characterized by the tendency to swell in cold water, particularly at the higher levels of treatment (3 to 4%), and by a lower gelatinization temperature than the base starch. The effect of increasing treatment level on swelling and gelatinization temperature is illustrated in Table 1.<sup>8</sup> The swelling test consists in suspending 25.0 g of starch in enough distilled water to give a volume of 100 ml, at pH 6.5, and letting the mixture stand in a 100-ml graduated cylinder for 16 hr at room temperature. The higher the volume of the starch layer, the more swollen the starch is. The gelatinization temperature can conveniently be determined by suspending 10.0 g of starch in 90 ml of distilled water in a cook-up beaker, placing the beaker in a boiling water bath while stirring with a thermometer, and recording the temperature at which the slurry begins to increase in viscosity and to become translucent.

The bulky hydrophilic succinate groups bring about a significant viscosity increase in corn starch. Neutral cooks of succinate starch derivatives are characterized by excellent

Table 1  
EFFECT OF SUCCINIC ANHYDRIDE  
TREATMENT ON COLD WATER  
SWELLING AND GELATINIZATION  
TEMPERATURE OF CORN STARCH

Treatment (%)	Cold water swelling (ml)	Gelatinization temp (°C)
0	34	72
1	35	67
2	40	65
3	47	63
4	49	58

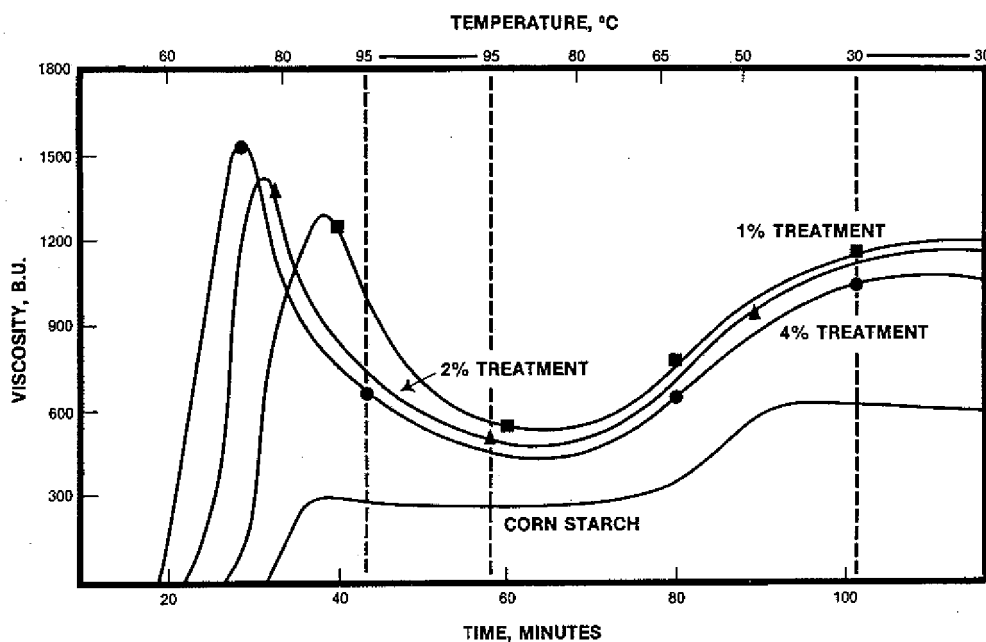


FIGURE 1. The effect of succinic anhydride treatment on the Brabender® viscosity of corn starch (5% anhydrous solids, pH = 6.5).

viscosity stability and clarity. These cooks show improved freeze-thaw stability.<sup>6</sup> Figure 1 illustrates the increase in the Brabender® viscosity of corn starch resulting from the succinic anhydride treatment.<sup>8</sup> The peak viscosity increases slightly with increasing treatment level while the final viscosity decreases since the low-temperature stability improves. Cooked corn starch forms a gel on cooling while the treated samples give smooth, stable high-viscosity colloidal suspensions. The corresponding gelatinization temperature, of course, drops with increasing treatment level. Unless otherwise indicated, the Brabender® procedure consisted in starting at 30°C, heating to 95°C at the rate of 1.5°C/min, holding 15 min at 95°C, cooling to 30°C at 1.5°C/min, and finally holding at 30°C for 15 min. Brabender® solids were 5% anhydrous.

As expected, pH affects the neutralization state of the carboxylic acid group of the derivative. The higher the pH, the greater the number of carboxyl groups in the hydrophilic carboxylate salt form. Therefore the pH of the starch has a significant effect on the Brabender® viscosity of the succinate derivative. This is illustrated in Figure 2 which shows



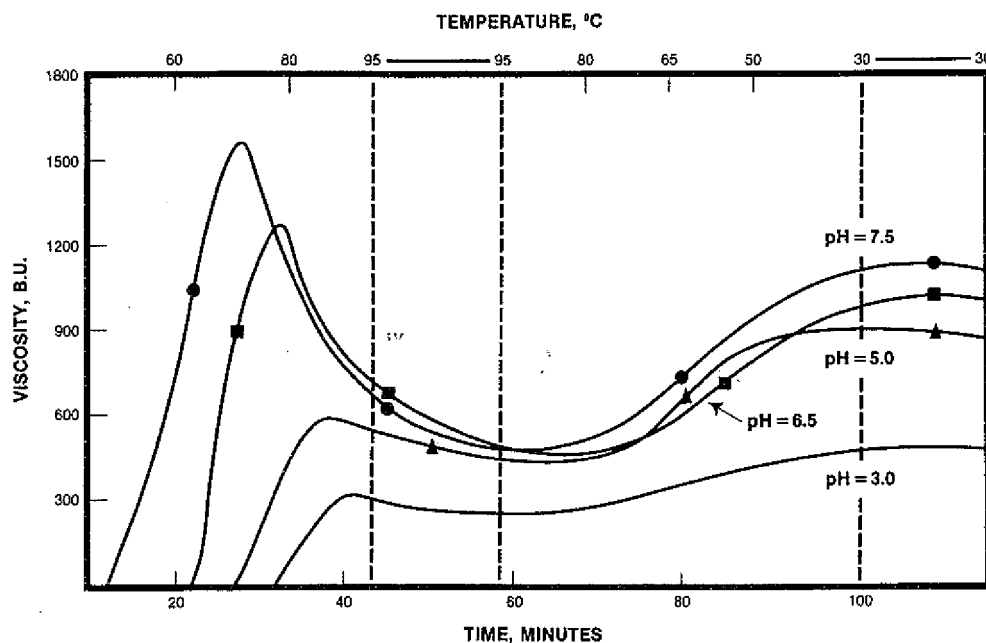


FIGURE 2. Effect of pH on Brabender® viscosity of corn starch treated with 3% succinic anhydride (5% anhydrous solids).

Brabender® amylographs at various pHs of corn starch succinate made by treatment with 3% succinic anhydride.<sup>8</sup> You will note that maximum viscosity is obtained at the near neutral pH. At pH of 5.0 the peak, as well as final viscosity, have dropped considerably. At pH below 5 some degradation of the starch molecules starts to occur. At pH of 3 the drop in viscosity is significant. Naturally, the fact that at lower pH the substituent group exists mostly in the acid form, which is less hydrophilic than the salt form, contributes considerably to the drop in viscosity. At pHs higher than 7.5, deesterification could become a problem and the benefits of succinate groups on the starch molecules would be lost.

Succinate derivatives of starch are anionic polyelectrolytes. Therefore solution viscosities are greatly affected by the presence of salt, such as sodium chloride. This is illustrated in Figure 3 with Brabender® viscosity profiles of corn starch treated with 3% succinic anhydride in distilled water and in 0.5 and 2% sodium chloride solution (w/v).<sup>8</sup> Note a substantial reduction in peak viscosity and a moderate loss in final viscosity in the presence of sodium chloride. The salt inhibits the swelling of the starch and this is also demonstrated by the increase in gelatinization temperature from about 60 to about 80°C.

Cooks of corn starch treated with succinic anhydride are relatively clear and stable of viscosity change, but are somewhat gummy in texture. Derivatives of waxy maize are clearer, but, depending on the treatment level, are more or less gummy in texture. For food applications such texture is generally undesirable. Therefore succinic anhydride can be reacted with lightly cross-linked granular starch so that the resulting texture of the cook is short, smooth, and shiny while the stability and much of the original clarity are retained. Cross-linking also improves the resistance of the derivative to breakdown at high temperature. Figure 4 shows the effect of light cross-linking (0.01% epichlorohydrin) on the viscosity profile of waxy corn starch treated with 3% succinic anhydride. In this case the Brabender® was held at 95 and 30°C for 30 min instead of 15 min.<sup>8</sup>

### C. Applications

Succinate derivatives offer a number of very desirable properties. These include low

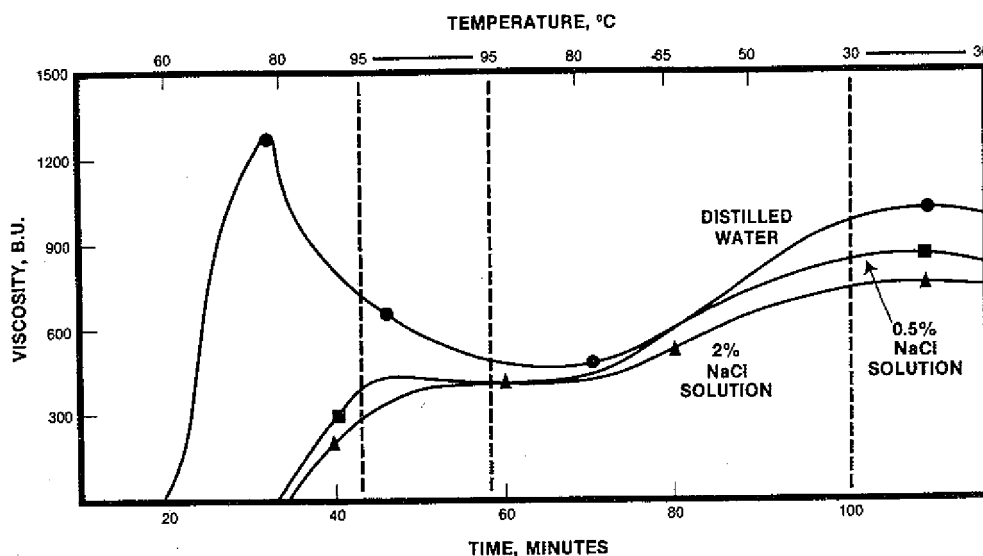


FIGURE 3. Effect of sodium chloride on Brabender® Amylograph of corn starch treated with 3% succinic anhydride (5% anhydrous solids, pH = 6.5).

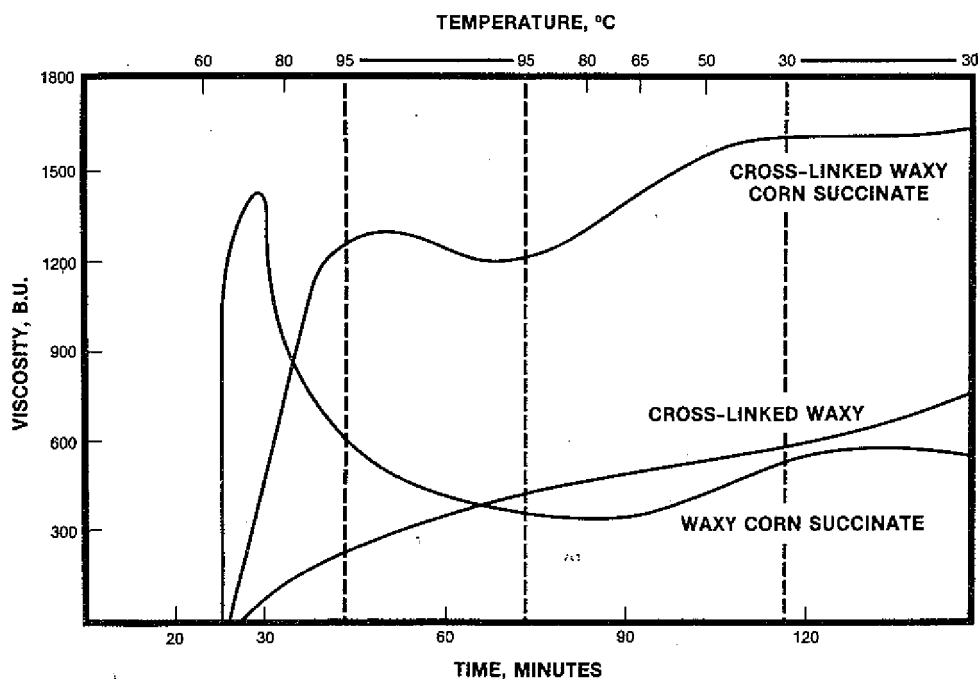


FIGURE 4. Effect of cross-linking on the Brabender® Amylograph of waxy corn starch treated with 3% succinic anhydride (5% anhydrous solids, pH = 6.5).

gelatinization temperature, high thickening power, low-temperature viscosity stability, and clarity of cooks. They also display good filming properties. These characteristics have made succinate derivatives of starch good candidates for a number of applications. In the food areas, succinate derivatives have been recommended as binders and thickening agents in soups, snacks, canned, and refrigerated food products. In the pharmaceutical area, succinate